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(54) PROCESS FOR THE PREPARATION OF KETONES
 AND/OR ALDEHYDES FROM OLEFINS

(71) We, STAMICARBON N.V., a Netherlands Limited Liability Company, of 2 van der Maesenstraat, Heerlen, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to catalysts for use in the preparation of ketones from olefins, to methods of preparation of such catalysts, and to the preparation of ketones from olefins using such catalysts.

It is known that olefins can be oxidized with the aid of catalysts to form aldehydes, ketones and acids. If the catalyst is sufficiently active at low temperatures, the equilibrium will be shifted in the presence of steam to favour the formation of ketones.

It is also known that the activity of a catalyst is not solely determined by the chemical composition thereof, but is also determined by the nature of the catalyst surface, and the present invention is directed to the use of a particular class of catalysts having characteristics hereinafter described.

The invention provides a catalyst for use in the preparation of a ketone from an olefin in the presence of oxygen and steam, which catalyst comprises particulate support material carrying at least one oxide of molybdenum, tungsten or vanadium and at least one oxide of tin, iron or titanium, the said oxide or oxides of tin, iron or titanium being homogeneously distributed over the support material in the form of particles at least a predominant proportion of which have a diameter of not more than 50 Å.

The catalyst according to the invention may be prepared by a method which comprises forming a mixture containing particulate catalyst support material and a solution contain-

ing ions of tin and/or iron and/or titanium, agitating the mixture form a suspension of the support material and making available hydroxyl ions in the suspension by an in situ generation of hydroxyl ions at such a low and controlled rate that a precipitate of material containing tin and/or iron and/or titanium is formed on the support material and not in the body of the solution, adding at least one salt or oxide of molybdenum, tungsten or vanadium to the suspension whereby material containing molybdenum and/or tungsten and/or vanadium is deposited on the support material, separating the thus-loaded support material from the suspension, and drying and calcining the separated loaded support material.

The invention further provides a process for the preparation of acetone from propylene, which process comprises contacting acetone with oxygen and steam in the presence of a catalyst according to the invention, and a process for the preparation of butanone from a butene, which process comprises contacting a butene with oxygen and steam in the presence of a catalyst according to the invention.

In the preparation of the catalyst, the gradual in situ generation of hydroxyl ions may be effected by the presence of urea in the suspension; such generation may be effected, for example, by adding urea to the suspension and subsequently heating the resulting suspension with intensive stirring until the required amount of the desired material has precipitated onto the support material with homogeneous distribution.

Instead of using urea to provide the gradual in situ generation of hydroxyl ions, any other compound which reacts with water to slowly release hydroxyl ions, e.g. sodium nitrite or hexamethylenediamine, may be used.

To obtain minute iron oxide particles on

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the surface of the support material, a soluble ferrous compound is preferably used, i.e. the solution contains ferrous ions.

- 5 The invention is illustrated by the following Examples which exemplify the preparation of:

1. Acetone from propylene, and
2. Methyl ethyl ketone (butanone) from butene.

10 1. ACETONE FROM PROPYLENE.

- To demonstrate the advantages of the present invention, propylene in combination with air and steam was passed over catalysts at various temperatures, and the reaction products thus obtained were analysed to determine the yield of acetone obtained and the selectivity of the various catalysts used.

- Catalysts identified as A, B, C, D and E were prepared in the manner set forth below. Catalysts A, B, C and D are comparative catalysts not in accordance with the invention; catalyst E is a catalyst according to the invention.

- In the preparation of catalysts A to C large particles of tin dioxide were used. The use of an inert support material, as required to provide and to stabilize catalysts containing small particles of tin dioxide, was not necessary, and hence in order to avoid dilution of the catalyst, no support material was used.

- Catalysts D and E contain small particles of tin dioxide, and hence support material having a high surface area was used.

- The preparation of the catalysts, including Catalyst E according to the invention, was effected as follows:

- A. 5 g. tin dioxide having a specific surface area of 3 sq. metres per gram and 2.5 g. MoO_3 were suspended in 100 ml. of water. The resulting suspension was filtered to provide a solid which was washed and dried at 450°C . Thereafter the resulting mass was treated in a reactor with steam at 475°C for 16 hours to provide a catalyst in which the tin dioxide particles had a mean diameter of about 2×10^3 Å.
- B. 5 g. tin dioxide having a specific surface area of 3 sq. metres per gram were loaded with $\text{MoO}_2(\text{OH})_2$ in a reactor by passing steam containing $\text{MoO}_2(\text{OH})_2$ and at 450°C over the tin dioxide for 45 hours.
- C. Particles of tin dioxide having a specific surface area of 25 sq. metres per gram

were obtained by treating granulated tin with nitric acid, drying and heating at 500°C . Electron microscopy showed that the particles of tin dioxide had a mean diameter of 250 Å. Subsequently the particles of tin dioxide were loaded with $\text{MoO}_2(\text{OH})_2$ in a reactor by passing steam containing $\text{MoO}_2(\text{OH})_2$ and at 450°C over the particles of tin dioxide for 40 hours.

- D. 75 g. "Acrosil" (Registered Trade Mark) silica (prepared by flame hydrolysis of SiCl_4) were suspended in a solution containing 11.4 g. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. After the pH of the resulting suspension had been adjusted to 7 by means of ammonia, 20 g. MoO_3 were added thereto. The suspension was filtered to provide a solid which was dried and calcined at 450°C to provide a catalyst which analyzed, by weight, 4.2% SnO_2 ; 20.4% MoO_3 ; and 75.4% SiO_2 . The particles of tin oxide were heavily conglomerated, the size of the conglomerates being greater than 100 Å. The conglomerates were covered by a monomolecular layer of a molybdenum compound.

- E. Catalyst according to the invention was prepared by suspending 75 g. "Acrosil" silica in a solution of 11.4 g. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in one litre of water. 19.4 g. urca were added to the resulting suspension which then was boiled with intensive stirring until a pH value of 7 was obtained. After the suspension had cooled, 20 g. MoO_3 were added thereto with stirring. The suspension was then filtered to provide a solid which was washed with 500 ml. of water. The washed material was calcined at 550°C . Electron microscope examination revealed that the tin oxide had been homogeneously applied to the support material as particles having a mean size of 10 Å. These particles were covered by a molecular layer of a molybdenum compound. The calcined material analyzed, by weight, 4.2% SnO_2 ; 20.4% MoO_3 ; and 75.4% SiO_2 .

Acetone was prepared from propylene in the presence of oxygen and steam in a first series of runs using catalysts A, B and E under conditions of low degree of propylene conversion and high catalyst temperature. The results are shown in Table I.

TABLE I

Catalyst	A	B	E
Mean temperature of catalyst °C	348	342	350
Conversion of propylene, %	5.2	4.5	1.1
Selectivity, %			
decomposition to CO and CO ₂	7	10	—
acetone	43	30	65
acetic acid	37	49	9.7
acrolein	6	2.5	14
acrylic acid	1	1.5	—
maleic acid	2	4	—
acetaldehyde	4	3	11

In view of the high activity of catalyst E, it was necessary, in order to obtain a low degree of conversion comparable with that obtained with catalysts A and B, to use a contact time which was short by a factor of about 10 of the contact time used with catalysts A and B. With this short contact time the conversion with catalyst E proved to be 4 to 5 times lower than with catalysts A and B.

Table II shows the results of a second series of similar runs using catalysts C and E under conditions of low degree of propylene conversion and low catalyst temperature.

TABLE II

Catalyst	C	E
Mean temperature of catalyst, °C	272	275
Conversion of propylene, %	5.0	4.8
Selectivity, %		
decomposition to CO and CO ₂	19	9.1
acetone	47	81
acetic acid	24	4.6
acrolein	0.2	—
acrylic acid	0.6	0.5
maleic acid	4	—
acetaldehyde	5	5

Table III shows the results of a third series of similar runs using catalysts D and E under conditions of high degree of propylene conversion and high catalyst temperature.

TABLE III

Catalyst	D	E
Mean temperature of catalyst, °C	340	340
Conversion of propylene, %	85	97
Selectivity, %		
decomposition to CO and CO ₂	29.5	21.8
acetone	4.7	21.4
acetic acid	49.5	42.5
acrolein	2.4	3.7
acrylic acid	1.2	0.2
maleic acid	9.4	6.1
acetaldehyde	3.5	4.6

It is deduced from the foregoing runs that:

1. The manner in which SnO₂ is loaded with molybdenum oxide does not influence the results; compare catalyst A with catalyst B in Table I.
2. Catalysts of the same overall chemical composition do not produce the same results; compare, in Table III, catalyst D with catalyst E.
3. As shown in Table III, the degree of conversion is considerably higher with catalyst E (97 % than with catalyst D (85 %) and the acetone production is increased fourfold.
4. The formation of CO, CO₂ and acetic acid is materially lower with catalyst E than with the other catalysts, particularly at low degrees of conversion.
5. The selectivity for the formation of acetone is more favourable with catalyst E than with the other catalysts, both at a low and at a high degree of conversion, as may be seen from Tables I, II and III.
6. The selectivity for the formation of acetone with catalyst E at low temperatures is especially favourable, as may be seen from Table II.

2. METHYL ETHYL KETONE (BUTANONE) FROM BUTENE.

In these experiments, a butene, air and steam were passed over catalyst present in a reactor under reaction conditions which

varied from experiment to experiment and which are as specified in Tables IV to VIII. The reaction product obtained was analyzed, special attention being paid to the determination of the yields of butanone, acetaldehyde, acids and the combustion products CO and CO₂.

The catalysts used were prepared by the process according to the present invention. One of the catalysts employed was prepared as follows: 74 g of "Aerosil" silica were suspended in a solution of 15.0 g. SnCl₄·5H₂O in one litre of water. Subsequently, 25 g of urea were added to the suspension which then was boiled, with vigorous stirring, until a pH-value of 7 had been reached. After the suspension had cooled, 25 g of MoO₃ were added thereto with stirring. The suspension was then passed through a filter to provide a solid which was washed with 500 ml of water and thereafter calcined at 450°C. Electron microscope examination of the solid showed that the tin oxide was homogeneously distributed over the silica in the form of particles having an average diameter of 10 Å. Said particles were covered with a monomolecular layer of a molybdenum compound by passing steam at 450°C over the solid for 16 hours. Under these conditions, the molybdenum oxide volatilizes and deposits on the tin oxide. The resulting catalyst analyzed, by weight, 7.4% SnO₂; 15.3% MoO₃; and 77.3% SiO₂. Other catalysts used in the experiments were prepared by similar methods according to the invention.

The results of the experiments are shown in Tables IV to VIII.

TABLE IV

Experiment No.	52	80
Butene	1	2
Butene : air : steam	1 : 14 : 9	1 : 16 : 11
Temp. of catalyst (°C)	228	224
SnO ₂ content of catalyst (%)	7.4	7.4
Space velocity (hr ⁻¹)	2200	2390
Conversion (%)	4.5	7.4
Selectivity (%)		
CO + CO ₂	18.7	11.8
butanone	47.0	52.8
acetaldehyde	8.9	11.1
acetic acid	13.0	15.1
acetone	2.8	2.2
methacrolein	1.3	0.7
maleic acid	8.7	5.1
formic acid	0.2	1.2

TABLE V

Experiment No.	70	69	68	71	75	74	73	76
Butene	1	1	1	1	2	2	2	2
Butene : air : stream	1 : 15 : 12	1 : 17 : 13	1 : 15 : 11½	1 : 15 : 12	1 : 14½ : 22	1 : 14½ : 22	1 : 14½ : 11	1 : 15½ : 11½
SnO ₂ content of catalyst (%)	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4
Temp. of catalyst (°C)	153	154	154	152	154	153	154	153
Space velocity (hr ⁻¹)	650	1370	2560	3900	650	1270	2390	3810
Conversion (%)	1.9	0.87	0.51	0.42	2.15	1.08	0.89	0.84
Selectivity (%)								
CO + CO ₂	19.0	—	—	—	4.95	8.2	9.1	6.2
butanone	71.5	87.5	82.5	89.0	82.4	76.3	76.6	84.0
acetaldehyde	2.2	2.1	1.6	1.7	7.7	8.25	7.6	5.3
acetic acid	3.9	6.1	10.2	5.5	3.0	4.9	4.4	2.6
acetone	—	—	—	—	0.7	0.55	0.5	0.9
methacrolein	2.2	2.5	2.4	2.4	—	—	—	—
maleic acid	1.0	1.4	2.6	1.4	1.0	1.5	1.4	0.8
formic acid	0.2	0.3	0.7	0.3	0.3	0.4	0.4	0.2

TABLE VI

Experiment No.	43	45	47	48	49	77	78	79	80	81
Butene	1	1	1	1	1	2	2	2	2	2
Butene : air : steam	1:14:6	1:14:6	1:14:6	1:14:6	1:14:6	1:15:9½	1:15:9½	1:15:9½	1:15:9½	1:14:9½
SnO ₂ content of catalyst (%)	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4
Temp. of catalyst (°C)	155	208	233	254	268	157	179	197	224	259
Space velocity (hr ⁻¹)	2000	2000	2000	2000	2000	2390	2390	2390	2520	2390
Conversion (%)	0.48	1.42	2.75	5.6	6.4	1.6	3.5	4.1	9.6	11.4
Selectivity (%)										
CO + CO ₂	0.0	28.9	29.6	34.4	39.1	0.0	11.4	10.0	35.6	31.0
butanone	74.0	49.3	40.4	33.6	29.2	86.5	72.5	68.1	39.6	26.8
acetaldehyde	2.7	6.3	9.8	13.8	14.1	8.6	8.25	9.05	8.3	10.0
acetic acid	14.3	8.7	10.9	9.2	8.0	2.9	4.4	7.4	10.2	20.2
acetone	0.7	1.7	2.9	3.4	3.5	0.9	1.25	1.75	1.7	2.2
methacrolein	2.0	1.8	2.0	2.0	3.0	0.1	0.5	0.5	0.5	1.4
maleic acid	5.2	2.6	3.4	2.9	2.5	0.9	1.5	2.4	3.4	6.7
formic acid	1.3	0.6	0.8	0.7	0.6	0.2	0.4	0.6	0.8	1.7

TABLE VII

Experiment No.	77	128	113
Butene	2	2	2
Butene : air : stream	1 : 15 : 9½	1 : 15 : 10½	1 : 16 : 11½
SnO ₂ content of catalyst (%)	7.4	18.0	43.8
Temp. of catalyst (°C)	157	163	158
Space velocity (hr ⁻¹)	2390	2320	2220
Conversion (%)	1.6	4.6	3.05
Selectivity (%)			
CO + CO ₂	0.0	9.0	13.4
butanone	86.5	69.5	76.1
acetaldehyde	8.6	7.1	5.6
acetic acid	2.9	9.8	2.9
acetone	0.9	0.7	0.8
methacrolein	0.1	—	—
maleic acid	0.9	3.2	1.2
formic acid	0.2	0.8	0.2

TABLE VIII

Experiment No.	66	65	64	67	128	133	138
Butene	1	1	1	1	2	2	2
Butene : air : stream	1 : 30 : 22	1 : 15½ : 13	1 : 8.7 : 7	1 : 3.6 : 3.3	1 : 14½ : 10½	1 : 14½ : 2.4	1 : 14½ : 0.7
SnO ₂ content of catalyst (%)	7.4	7.4	7.4	7.4	18.0	18.0	18.0
Temp. of catalyst (°C)	246	249	252	255	163	163	130
Space velocity (hr ⁻¹)	1310	1320	1380	1620	2320	1560	1470
Conversion (%)	16.0	10.8	7.9	3.54	4.6	6.9	1.2
Selectivity (%)							
CO + CO ₂	29.4	27.2	29.6	20.9	9.0	6.5	0
butanone	26.1	32.6	36.2	52.3	69.5	66.0	80.5
acetaldehyde	8.8	9.4	8.5	9.9	7.1	13.5	14.4
acetic acid	22.9	21.9	17.6	11.4	9.8	8.6	3.2
acetone	2.2	2.0	2.0	2.4	0.7	2.1	0.6
methacrolein	1.2	1.3	1.3	2.4	—	—	—
maleic acid	6.4	5.5	4.9	—	3.2	2.7	1.0
formic acid	3.3	0.1	1.2	1.0	0.8	0.7	0.2

In Tables IV and V the results of experiments using butene-1 and butene-2 are compared. It appears that the reactivity of butene-2 is greater than that of butene-1; the conversion is distinctly higher in the experiments with butene-2. Since there is no appreciable difference between butene-1 and butene-2 in so far as the butanone yields are concerned, it is preferred that butanone is prepared from butene-2 by the process according to the invention.

In Table V, the influence of the space velocity is shown both for butene-1 and for butene-2. The conversion is greater at lower space velocities; in the case of butene-2, the formation of CO and CO₂ does not appreciably increase with increase in the degree of conversion.

Table VI shows the influence of the catalyst temperature in the various experiments. With both butene-1 and with butene-2, the degree of conversion increases with increase in temperature; this is attended with a decrease in the yield of butanone and an increase in the yields of CO and CO₂. At higher temperatures, butene-1 yields more acetaldehyde and butene-2 yields more acetic acid. According to a preferred feature of the invention, the preparation of butanone and/or acetaldehyde from butene is effected at a temperature of from 125 to 300°C. If it is desired that butanone is formed as the main product, a temperature of from 125 to 200°C is preferably employed; if acetaldehyde is desired as one of the products, a temperature above 200°C is preferably employed.

Table VII shows the effect of the tin dioxide content of the catalyst. With use of the catalysts containing 18.0 and 43.8% by weight tin dioxide, the degree of conversion is distinctly higher than in the case of the use of the catalyst having a tin dioxide content of 7.4% by weight. The somewhat higher degree of conversion achieved with the use of catalyst containing 18.0% by weight tin dioxide is due to the somewhat higher reaction temperature employed, viz. 163°C as compared to the temperature of 158°C which was employed in the use of the catalyst having a tin dioxide content of 43.8% by weight. As in the other experiments, the butanone yield decreases slightly when the degree of conversion is kept relatively high.

Table VIII shows the influence of the butene/air/steam ratio. In the case of butene-1, the degree of conversion increases with increase in the proportion of steam employed, the yield of acetic acid increasing at the expense of butanone. The conversion of butene-2 as a function of the amount of steam employed shows a maximum when the latter is comparatively small. It is noteworthy that if, at a low reaction temperature, the amount of steam employed is smaller than the amount of butene employed, a higher

selectivity towards the formation of butanone is obtained; operation in such manner is a preferred feature of the process according to the invention. Heat losses can thus be restricted and it is attractive to recycle the product flow in industrial applications of the process according to the invention.

WHAT WE CLAIM IS:—

1. A catalyst for use in the preparation of a ketone from an olefin in the presence of oxygen and steam, which catalyst comprises particulate support material carrying at least one oxide of molybdenum, tungsten or vanadium and at least one oxide of tin, iron or titanium, the said oxide or oxides of tin, iron or titanium being homogeneously distributed over the support material in the form of particles at least a predominant proportion of which have a diameter of not more than 50 Å.

2. A method of preparing a catalyst according to Claim 1, which method comprises forming a mixture containing particulate catalyst support material and a solution containing ions of tin and/or iron and/or titanium, agitating the mixture to form a suspension of the support material and making available hydroxyl ions in the suspension by an in situ generation of hydroxyl ions at such a low and controlled rate that a precipitate of material containing tin and/or iron and/or titanium is formed on the support material and not in the body of the solution, adding at least one salt or oxide of molybdenum, tungsten or vanadium to the suspension whereby material containing molybdenum and/or tungsten and/or vanadium is deposited on the support material, separating the thus-loaded support material from the suspension, and drying and calcining the separated loaded support material.

3. A method according to Claim 2, in which the suspension further comprises urea and in which the hydroxyl ions are made available in the suspension by hydrolysis of said urea.

4. A method according to Claim 2 or Claim 3, in which the solution contains ferrous ions.

5. A method of preparing a catalyst as claimed in Claim 2, substantially as hereinbefore described.

6. A catalyst prepared by a method according to any of Claims 2 to 5.

7. A process for the preparation of acetone from propylene, which process comprises contacting acetone with oxygen and steam in the presence of a catalyst as claimed in Claim 1 or Claim 6.

8. A process for the preparation of butanone from a butene, which process comprises contacting a butene with oxygen and steam in the presence of a catalyst as claimed in Claim 1 or Claim 6.

9. A process according to Claim 8, in which the butene is butene-2.

10. A process according to Claim 8 or

Claim 9, in which the said contacting is effected at a temperature of from 125 to 300°C.

- 5 11. A process according to Claim 9 or Claim 10, in which the amount of steam employed is smaller than the amount of butene-2 employed.

12. Acetone prepared by a process according to Claim 7.

13. Butanone prepared by a process according to any of Claims 8 to 11. 10

HYDE & HEIDE,
110 Bishopsgate, London, E.C.2.
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Agents for the Applicants.

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